The Borides of Some Transition Elements

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Reprinted from

ACTA CHEMICA SCANDINAVICA 4 (1950) 209—227

Uppsala

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The Borides of Some Transition Elements

Inaugural Dissertation

by

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By due permission of the Philosophical Faculty of the University of Uppsala, to be publicly discussed in the lecture hall of the Institute of Chemistry, April 22, 1950, at 10 a. m., for the degree of Doctor of Philosophy. In addition to this survey the papers numbered 1—6 and 24 in the list of references will be publicly discussed.

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The Borides of Some Transition Elements

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In 1945, the author started an investigation on the borides of the transition elements. During the years 1945—1949 a great number of binary systems between transition elements and boron have been studied. The investigations have been reported in this journal [1–6] and include the metals chromium, manganese, nickel, zirconium, columbium, molybdenum, tantalum, tungsten, and thorium. They have mainly been concentrated on phase analyses and structure determinations of the intermediary phases. In the present paper a survey of the results will be given, including a discussion of the structures. Some boride structures reported by other investigators are included in the discussion.

EARLIER INVESTIGATIONS

The earlier investigations on borides often are of questionable value, mainly because of the unsatisfactory methods of preparation, the impurity of commercial boron used as starting material, and the great difficulties of isolating and studying the intermediary phases by classical chemical methods. References to these previous works are found elsewhere [7–8]. Some investigations by means of X-ray methods are reported for the iron-, cobalt-, nickel-, and titanium-boron systems [9–12], on the borides of composition MeB_2 [13–15] and MeB_6 [16–19] and on some miscellaneous borides [20–23]. Some of the results have been critically discussed by the present author [1–6].

METHODS OF PREPARATION AND INVESTIGATION, INCLUDING A METHOD FOR PREPARING BORON OF HIGH PURITY

Earlier investigators have used different methods for preparing metal borides, *e. g.* electrolysis of fused salt baths, containing oxides of metal and boron, reduction of oxide mixtures with carbon, and direct synthesis from the

elements. Of these methods, the last seemed to be the most accurate and was used in these investigations. The main problems connected with this method are the great difficulties of getting pure starting materials and of reaching the high temperatures under controlled conditions, which are necessary for the syntheses. The transition metals used were either commercially obtainable in a pure state or could easily be purified. Commercial boron, however, has a content of only 65—80 % of boron. Several methods have been used in order to get pure boron; references are found elsewhere [24]. The methods described only give very small amounts. In order to obtain greater amounts, a new method for preparing boron with a purity of 98—99 % was developed by the author [24]. It consists essentially of the vapour phase reduction of boron tribromide with hydrogen in a silica tube at 750—800° C.

The borides were prepared by sintering or melting the constituents together. This was either done in evacuated silica tubes at 1 100—1 200° C or in vacuum furnaces at 1 200—2 000° C. Two different vacuum furnaces were used, a resistance furnace with a graphite tube as heating element or a high frequency induction furnace. Both were constructed for this investigation and are described elsewhere [25–26].

The usual method of investigation was to heat mixtures of metal and boron in different proportions. Phase analyses of the products were carried out by X-ray methods, and selected alloys were chemically analyzed. The structures of the pure phases were determined by powder or by single crystal methods. More details about the X-ray work are found in the reference papers [1–6].

STRUCTURES OF THE INTERMEDIARY BORIDE PHASES

A general tendency of the boron atoms to form chains, nets, or three-dimensional frameworks with increasing boron content of the systems has been found. The structures will be discussed on the basis of the boron arrangement.

Radius of the boron atom. From phases with small metal atoms, in which a metal-boron or boron-boron contact probably exists, the radius of the boron atom was found to be 0.86—0.88 Å. 0.87 Å may be accepted as a mean value, in close agreement with 0.86 Å, reported for boron in CaB_6 [19], which seems to be the most reliable value from earlier experiments. Distances less than 2×0.86 Å between part of the boron atoms have been observed only for one type of boride phases, the borides with double chains of boron atoms (Table 6). This shortening probably results from the formation of double bonds.

Solubility of boron in the undistorted metal lattice. Solubility of boron was observed in thorium, α-zirconium and in tantalum at higher temperatures.

Table 1. Me_2B-borides of the $CuAl_2$-type.

Metal	r_B/r_{Me}*	a (Å)	c (Å)	c/a	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)
Ta	0.60	5.778	4.864	0.84	2.73	2.47	2.43
W	0.62	5.564	4.740	0.85	2.68	2.38	2.37
Mo	0.63	5.543	4.735	0.85	2.67	2.37	2.37
Mn	0.69	5.148	4.208	0.82	2.37	2.20	2.10
Fe	0.69	5.109	4.249	0.83	2.41	2.18	2.12
Co	0.69	5.016	4.220	0.84	2.37	2.15	2.11
Ni	0.70	4.990	4.245	0.85	2.36	2.14	2.12

* For calculating the radius ratio the values $r_B = 0.87$ Å and r_{Me} = the value for twelvefold coordination of the metal, given by Pauling [31], have been used. The interatomic distances given in the tables contain a few small corrections compared with the original papers.

According to Ehrlich [12], boron is also soluble in α-titanium. For the other metals investigated no solubility was observed.

Borides with isolated boron atoms. To this group belongs a great number of borides of the $CuAl_2$-type (C 16) as well as the closely related δ-phase in the manganese-boron system (Tables 1 and 2). Both types consist of sheets of tetrahedra of metal atoms with boron atoms in the holes between these sheets (Fig. 1). Each boron atom is surrounded by eight metal neighbours at equal distances. For the borides of the $CuAl_2$-type, the radius of the holes varies for different metals between the limits 0.96 Å for nickel to 1.11 Å for tantalum, the boride of which was stable only at lower temperatures and for which the boron content was impossible to determine. For the other structure type with isolated boron atoms (δ Mn-B) the corresponding value 0.98 Å was found. In all the borides with isolated boron atoms, the holes thus are appreciably larger than the boron atoms, if these are assumed to have the radius 0.87 Å. A larger radius for boron in borides with isolated boron atoms than in other borides may thus be possible, but the great variation in the values indicates that the boron atoms are more loosely accomodated in these lattice types than in the other types.

Table 2. δ-phase in the Mn-B system.

Metal	r_B/r_{Me}	a (Å)	b (Å)	c (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)
Mn	0.69	14.53	7.293	4.209	2.41	2.19	2.11

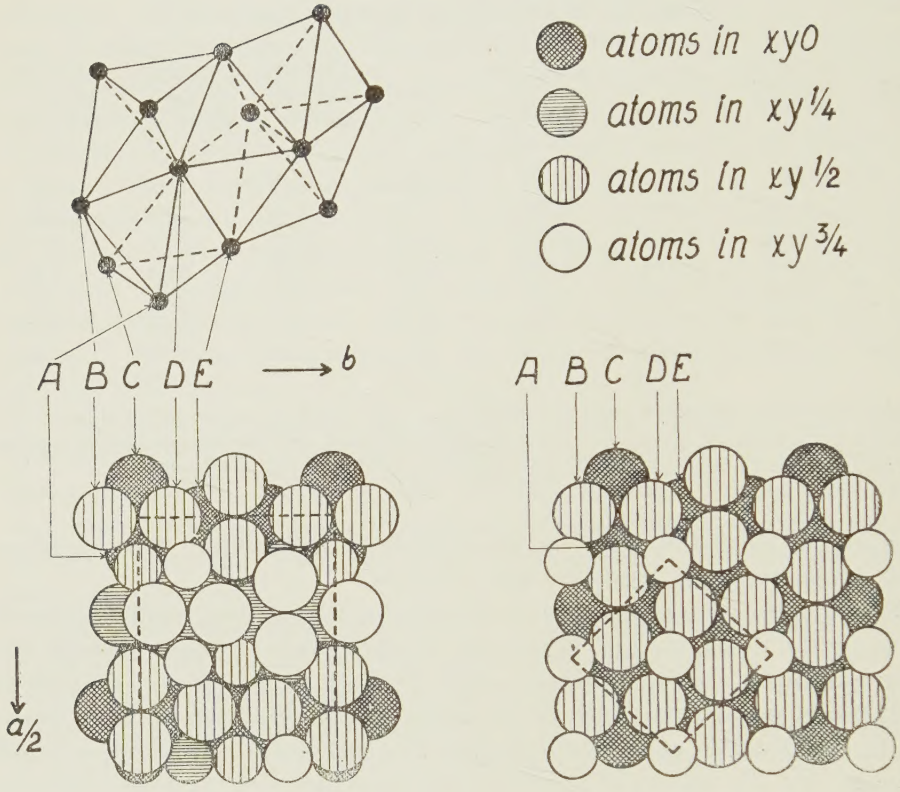

Fig. 1. Borides with isolated boron atoms. (Large circles represent metal atoms, small circles boron atoms.)
Left: δ-phase in the Mn-B system.
Right: Me_2B-borides of the $CuAl_2$-type.

Geometrically, the boron atoms are arranged in strings through the metal lattice. Thus for instance in the borides of the $CuAl_2$-type the boron-boron distance within a string is $c/2$ giving values of the boron-boron distance within the limits 2.11 Å (for cobalt) to 2.43 Å (for tantalum). The distances between nearest boron atoms in different strings is considerably larger (*e. g.* 3.55 for cobalt, 4.09 for tantalum). Also the geometrical arrangement of the boron atoms in the δ-phase in the manganese-boron system is that of strings. The boron-boron distance in a string is 2.11 Å, whereas the distance between nearest boron atoms in different strings is 3.63 Å. The boron atoms in these phases have been regarded as not forming any boron-boron bonds, but the string formation may indicate a tendency for boron-boron bond formation.

Table 3. MeB-borides of the FeB-type.

Metal	r_B/r_{Me}	a (Å)	b (Å)	c (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	Angle between the boron bonds
Mn	0.69	5.560	2.977	4.145	2.67	2.19	1.80	112°
Fe	0.69	5.506	2.952	4.061	2.63	2.15	1.80	110°
Co	0.69	5.253	3.043	3.956	2.60	2.12	1.86	110°

Param. x_B and z_B 0.031 and 0.620 (FeB), 0.037 and 0.625 (CoB). Bjurström's values slightly changed [9].

Table 4. MeB-borides of the MoB-type.

Metal	r_B/r_{Me}	a (Å)	c (Å)	c/a	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	Angle between the boron bonds
W	0.62	3.115	16.93	5.44	2.86	2.23	1.74	127°
Mo *	0.63	3.110	16.95	5.45	2.86	2.23	1.74	127°

* The axes of MoB in the original paper [1] have been given with the values a = 3.105, c=16.97 Å. These, however, are the values at the lower limit of the homogeneity range (48.8 atomic % boron). The values, given in Table 4, are those obtained for a boride with 50 atomic % boron.

Table 5. MeB-borides of the CrB-type.

Metal	r_B/r_{Me}	a (Å)	b (Å)	c (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	Angle between the boron bonds
Ta	0.60	3.276	8.669	3.157	2.90	2.40	1.86	116°
Cb	0.60	3.298	8.724	3.166	2.92	2.42	1.86	117°
Cr	0.69	2.969	7.858	2.932	2.65	2.19	1.74	115°

Borides with boron chains. Three structure types with the boron atoms forming zig-zag chains have been observed (Tables 3—5). They are closely related to each other. The metal lattices may be regarded as consisting of trigonal prisms connected in different ways, for instance as in Fig. 2. Channels appear through which boron chains are extended in the lattices. Each boron atom is situated in the centre of a trigonal prism of metal atoms and in contact with six metal atoms with their centres at the corners of the prism. A seventh metal atom is situated at a slightly larger distance outside the prism. Each boron atom is also in contact with two other boron atoms.

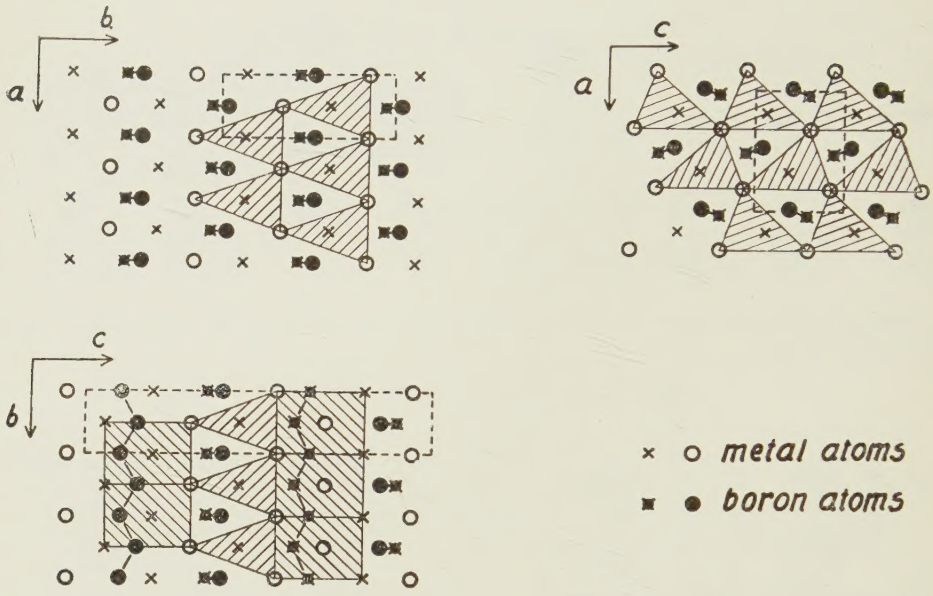

Fig. 2. Projections of boride structures with boron chains. (Circles and crosses are situated at levels 1/2 apart.)
Above left: CrB-type.
Below left: MoB-type.
Right: FeB-type.

The borides of the FeB- and CrB-types seemed to have the fixed composition MeB, whereas those of the MoB-type showed an extended homogeneity range, extending slightly on both sides of the ideal composition MeB (48.8< "MoB"<51.5 atomic % boron, 48.0<"WB"<50.5 atomic % boron). For both these borides, the *a*-axes increase and the *c*-axes decrease with increasing boron content.

There are several possibilities for the explanation of the extended homogeneity ranges. A possibility for a phase with a higher boron content than 50 atomic % would be a lattice in which some of the metal atoms are missing or their positions occupied by boron. Such a lattice is less probable for these borides, however, as a decrease of both *a*- and *c*-axes with increasing boron content would result.

Metal atoms may also occupy positions in the channels, positions which are normally occupied by boron. A phase with such a lattice would exist only for a lower boron content than 50 atomic %, but this alternative may be excluded as the *a*-axis of such a hypothetical lattice would decrease with increasing boron content of the phase.

A third alternative, which already has been suggested by the present author [1], is a variation of the number of boron atoms in the channels. Such a variation would probably be reflected in a variation of the axes of the unit cell in accordance with the observations (this will be clear if the boron-metal and metal-metal contacts of the lattice are considered, Fig. 2). In an ideal MoB-lattice with a boron content of 50 atomic %, all the channels of the metal lattice must contain boron atoms. They are situated in the largest interstices of the channels, and each such interstice is occupied by a boron atom. For a boride with a lower boron content than 50 atomic %, the number of boron atoms per unit length in the channels will be lower than the number of interstices. This may be caused by vacancies in the places occupied by boron atoms at 50 atomic %. This leaves fragments of boron chains with their boron atoms still in the largest holes of the channels. Another possibility is the formation of extended chains, the angle between the boron bonds thus being increased and the boron atoms still being in contact through the whole channel. For such a chain, the largest interstices of the channel and the boron atoms of the chain would no longer be in phase, and the boron atoms would be forced to occupy interstices, which for an ideal phase are too small for a boron atom (the smallest holes of the channels having space for atoms with a radius of only 0.77 Å, compared with 0.87 Å for the largest). The result would be a lattice deformation of the metal, probably periodic.

For a phase with a higher boron content than 50 atomic %, a chain with a greater number of boron atoms per unit length than the number of "ideal" interstices and a uniform distribution of boron atoms over the whole chain is the only probable possibility. Also in this case a periodically expanded metal lattice is to be expected. The angle between the boron-boron bonds in the "compressed" chain would be less than the value for an "ideal" chain with its boron atoms in the largest interstices of the channels.

It is to be noted that the angles between the boron-boron bonds for the chains in the borides of the MoB-type are larger than the corresponding angles for the other borides with boron chains. The tendency for the boron-boron bonds to form a lower angle than in the borides of the MoB-type may be an explanation of the extension of the homogeneity ranges for this type of borides, an extension which has not been observed for the other borides with chains. This tendency would only account for the extension above 50 atomic %, however.

There is finally also a possibility that all the boron atoms are never situated in the largest interstices of the channels but they form chain fragments with a lower bonding angle than that corresponding to the boron atoms situated in the interstices. These chains would thus successively add more

Table 6. Me_3B_4 borides.

Metal	r_B/r_{Me}	a (Å)	b (Å)	c (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å) (in pair)	Distance B-B (Å) (in chain)
Ta	0.60	3.29	14.0	3.13	2.97	2.40	1.54	1.85
Cb	0.60	3.305	14.08	3.137	2.98	2.40	1.58	1.84
Mn	0.69	3.032	12.86	2.960	2.68	2.24	1.47	1.75
Cr	0.69	2.984	13.02	2.953	2.68	2.23	1.51	1.74

boron atoms over the homogeneity range. This possibility is less probable, as the composition MeB seems to be of special importance for the borides with chains.

A deformation of the metal lattice would probably influence the powder photographs in a visible way. A reinspection of these showed that for the molybdenum-boron phase a slight variation in the relative intensities for some reflections existed, if powder photographs from specimens with low and high boron content were compared (*e. g.* 2 1 3 compared with 1 1 10,2 1 5 compared with 2 0 8). The variations were too small to permit any accurate determinations or to draw any conclusions concerning the origin of these variations.

It is unquestionable, however, that for the borides of the MoB-type the number of boron atoms in the channels of the metal lattice varies. But it has not been possible to explain why the borides of the FeB- and CrB-types do not also show any extended homogeneity ranges or where in the channels the boron atoms are situated, when the boron content of the phase differs from 50 atomic %.

Borides with double chains (fragments of nets). In the borides of composition Me_3B_4 (Table 6), the boron atoms form double chains. The double chains may also be regarded as fragments of hexagonal boron nets, and these borides thus have an intermediate position between borides with boron chains and borides with simple boron nets (Fig. 3). The boron-boron distance in the

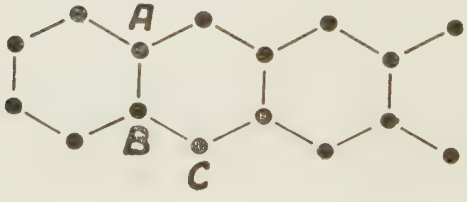

Fig. 3. Double chain of boron atoms.

Table 7. MeB_2-borides of the AlB_2-type.

Metal	r_B/r_{Me}	a (Å)	c (Å)	c/a	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	a_{Me} a_{Cr}	c_{Me} c_{Cr}
(Al)	0.61	3.00	3.25	1.08	3.00	2.38	1.73	1.010	1.060
Zr	0.54	3.169	3.530	1.11	3.17	2.54	1.83	1.067	1.151
Ti	0.59	3.028	3.228	1.07	3.03	2.38	1.75	1.020	1.053
Ta	0.60	3.078	3.265	1.06	3.08	2.41	1.78	1.037	1.065
Cb	0.60	3.089	3.303	1.07	3.09	2.43	1.78	1.040	1.077
V	0.65	2.998	3.057	1.02	3.00	2.31	1.73	1.010	0.997
Cr	0.69	2.969	3.066	1.03	2.97	2.30	1.71	—	—

Table 8. Me_2B_5-borides.

Metal	r_B/r_{Me}	a (Å)	c (Å)	c/a	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)
W	0.62	2.982 3.011	13.87 20.93	4.65	2.98	2.32	1.72
Mo	0.63	($r=7.190$, $\alpha=24°\ 10'$)		6.95	3.01	2.32	1.74

same half of a double chain (BC) was found to be about 2 r_B, whereas the distance between adjacent boron atoms in different halves always was found to be shorter, about 1.50 Å. This indicates a formation of boron pairs in which the boron atoms probably are connected by double bonds. (The double bond radius for boron is 0.76 Å according to Pauling.) The boron atoms of type "C" are surrounded by six+one metal atoms and two boron atoms in the

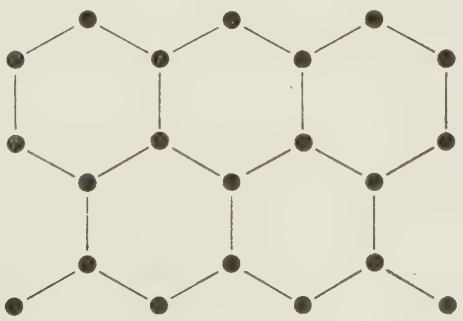

Fig. 4. Hexagonal net (H) of boron atoms.

same way as in the borides with boron chains. The boron atoms of type "B" are surrounded by six metal atoms at the same distance, situated at the corners of a trigonal prism, two boron atoms at the usual boron-boron distance and one boron atom at a shorter distance. All these borides had the fixed composition Me_3B_4; no extension of the homogeneity ranges was observed.

Borides with two-dimensional nets. The next step in the connection of the boron atoms, the formation of hexagonal boron nets (Fig. 4), was observed for several phases. Most of these borides belong to the AlB_2-type (*C* 32, Table 7). In the molybdenum- and tungsten-boron systems, there are phases with the ideal composition Me_2B_5, having more complicated structures (Table 8). The metal lattices of all these phases are closely related, and may be regarded as consisting of close-packed metal sheets (A, B, C) arranged in different ways. In analogy to the usual notation for hexagonal and cubic close-packings (A B A B and A B C A B C resp.), the sequence of metal sheets will be A A B B A A B B for the W_2B_5-type, A A B B C C A A B B C C for the Mo_2B_5-type, whereas the metal lattice for the AlB_2-type is simple hexagonal. A A A. Boron atoms are situated in the interstices between these metal sheets, either forming plane nets (H) with hexagonal meshes or slightly puckered sheets (K) formed by nets of the same kind as H but with additional boron atoms in the centres of some of the meshes. The phases may be described as sequences AHAHAH for the AlB_2-type, AHAKBHBKAHA for the W_2B_5-type, and AHAKBHBKCHCKAHA for the Mo_2B_5-type. For "CbB_2" and "TaB_2" of the AlB_2-type, extended homogeneity ranges were observed. They were extended on both sides of the ideal composition MeB_2, showing the existence of incomplete boron nets at lower boron contents than 66.7 atomic % and complete nets with additional boron atoms in the centres of the hexagonal meshes at higher boron contents [4]. A shortening of the boron-boron distance was observed when additional boron atoms were taken up in the meshes of the boron nets (H). A boron atom in a complete net (H) is surrounded by six metal atoms at equal distances situated at the corners of a trigonal prism with the boron atom in the centre, and three boron neighbours at the usual boron-boron distance.

Borides with three-dimensional boron frameworks. A great number of borides with composition MeB_6 have been reported, the metals also including some which are not transition elements [16–19] (Table 9). They are all isomorphous, and the metal atoms form a simple cubic lattice. X-ray studies on CaB_6($D\ 2_1$) have shown that all the boron atoms form a three-dimensional framework with the metal atoms in the interstices. The boron atoms form octahedra. Each boron atom has five boron neighbours at the same distance 1.72 Å, four in the same octahedron and one in a neighbouring. It also has four metal

Table 9. MeB_6-borides of the CaB_6-type.

Metal	r_B/r_{Me}	a (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	$(Me\text{-}B)_{obs}/(r_B + r_{Me})_{calc}$
(Ba)	0.39	4.29	4.29	3.16	1.78	1.02
(Sr)	0.40	4.20	4.20	3.09	1.74	1.03
(Ca)	0.44	4.153	4.15	3.06	1.72	1.08
Yb	0.45	4.14	4.14	3.05	1.71	1.09
La	0.47	4.153	4.15	3.06	1.72	1.12
Ce	0.48	4.137	4.14	3.05	1.71	1.13
Nd	0.48	4.126	4.13	3.04	1.71	1.13
Pr	0.48	4.129	4.13	3.04	1.71	1.13
Gd	0.48	4.13	4.13	3.04	1.71	1.14
Th	0.48	4.16	4.16	3.07	1.72	1.15
Y	0.48	4.08	4.08	3.01	1.69	1.13
Er	0.50	4.110	4.11	3.03	1.70	1.16

neighbours situated so that the four metal atoms and the boron atom form a tetragonal pyramid with boron at the apex and the four metal atoms forming the square base. The boron-metal distance, however, is considerably greater than the sum of the normal atomic radii, e. g. for cerium 3.05 compared with $r_B + r_{Ce} = 2.69$ and for thorium 3.07 compared with 2.67. This may in part depend on the high coordination number of the metal atoms, each metal atom being surrounded by twenty four boron neighbours and six metal neighbours. For those metals which are large enough to expand the boron framework (*e. g.* barium and strontium) the ratio $(r_B + r_{Me})_{obs}/(r_B + r_{Me})_{calc}$ is nearly constant (Table 9), indicating that the increase of the metal radius owing to the high coordination is about 2 % compared with Pauling's values for twelvefold coordination. For the other metals with smaller radii an increase of this ratio is noted, indicating that the boron atoms are in contact, forming a rather stable boron framework with metal atoms in the interstices. The metal-boron bonds are probably rather weak for the smaller metal atoms.

Table 10. Borides of the UB_{12}-type.

Metal	r_B/r_{Me}	a (Å)	Shortest distance Me-Me (Å)	Shortest distance Me-B (Å)	Shortest distance B-B (Å)	$(Me\text{-}B)_{obs}/(r_B + r_{Me})_{calc}$
U	0.57	7.473	5.28	2.79	1.76	1.17

Recently the structure of UB_{12}[23] has been reported (Table 10). The structure, closely related to that of the MeB_6 borides mentioned, is that of a three-dimensional boron framework with uranium atoms in the holes. Each boron atom has five boron neighbours at a distance of about 0.88 Å, and the value of the distance boron-uranium is greater than $r_B + r_U$ as for the MeB_6-borides.

Finally it is of interest to note that these borides, which are close to the boron side of the systems, follow Hume-Rothery's (8-N)-rule, which would give five neighbours for boron.

GENERAL DISCUSSION

The structure types described include all those borides of transition elements of which the structures have been determined. It is to be observed that with the methods used, usually only the positions of the metal atoms have been directly determined. The positions of the boron atoms have been determined from space considerations, assuming that boron atoms occupy the largest holes of the metal lattice. For some phases in the chromium- and manganese-boron systems it has been possible by Fourier methods to obtain boron maxima by studying suitable projections of the electron density. The locations of these maxima have always been in accordance with the results from space considerations and support the results for isomorphous borides of heavier metals.

The existence of boron-boron bonds. A general tendency for the boron atoms to form an increasing number of boron-boron contacts with increasing boron content of the phases has been found. These contacts may be only a consequence of a convenient space arrangement of the atoms or they may involve boron-boron bonds, probably of a covalent type. The experimental evidence clearly shows that the contacts are of bonding character. The fact that boron chains appear in three different types of metal lattices is itself a strong support for the existence of real bonds within the chains. If the axes of the orthorhombic unit cells of the isomorphous borides TaB and CrB are compared (Table 5), the ratios a_{Ta}/a_{Cr} and b_{Ta}/b_{Cr} are 1.103, whereas the ratio c_{Ta}/c_{Cr} is only 1.077. Comparing CbB and CrB the corresponding values are $a_{Cb}/a_{Cr} = 1.111$, $b_{Cb}/b_{Cr} = 1.110$ but $c_{Cb}/c_{Cr} = 1.080$. The lattice is thus expanding less in the direction of the *c*-axis, *i. e.* the direction of the boron chains, than in the other directions when going from the smaller chromium to the larger tantalum and columbium atoms. For the Me_3B_4-borides with double chains of boron atoms (Table 6), the ratios are $a_{Cb}/a_{Mn} = 1.090$, $b_{Cb}/b_{Mn} = 1.095$ and $c_{Cb}/c_{Mn} = 1.060$, the double chains all being extended in the *c*-direction. The variation of the parameter for the metal atoms, which occurs when going from

the smaller atoms of chromium and manganese to the larger atoms of columbium and tantalum ($y_{Cr} = y_{Mn} = 0.186$, $y_{Cb} = y_{Ta} = 0.180$), also verifies the existence of boron-boron bonds. The distance within the boron pair (A—B. Fig. 3) only increases from 1.47 to 1.58 Å for this variation of parameter, instead of increasing to 1.69 Å, as would occur if the parameter remained constant 0.186 (comparing manganese and columbium).

Similar effects are visible for the nets. In Table 7, the ratios a_{Me}/a_{Cr} and c_{Me}/c_{Cr} have been calculated for the different borides MeB_2 of the AlB_2-type. With increasing radius of the metal atom, the lattice is expanding more in the direction of the c-axis than in the direction of the a-axis (the only exception is for VB_2, the axial lengths of which have been taken from literature [15]). The boron nets are all arranged normal to the c-axis, making an expansion in the c-direction easier than in the a-direction when the radius of the metal atom increases. As has already been pointed out elsewhere by the author [4], a decrease of the boron-boron distance is noted (observed by the decrease of the distances between certain metal atoms) when additional boron atoms are taken up in the holes of an hexagonal boron net. The decrease is caused by the forces between the boron atoms of the rings and the additional atoms in the ring centres.

For the three-dimensional boron frameworks, as has already been pointed out, the increased boron-metal distance, compared with the normal radius sum, is an indication of a rigid boron framework.

The existence of boron-boron bonds has thus indirectly been verified. It has not been possible to determine directly the electron density within these boron bonds. This in part results from the low scattering power of boron compared with that of the metals, and in part from the effects of termination of the Fourier series, caused by the small number of reflections obtainable from these unit cells which are usually small and highly symmetrical.

Analogies between borides and hydrides, carbides and nitrides. Hydrides, borides, carbides and nitrides of the transition elements form a group of phases with characteristic properties, as was pointed out by Hägg [27–28]. These compounds have metallic properties. If the ratio of the radius of the non-metal (r_X) to the radius of the metal (r_{Me}) is less than 0.59, the small non-metallic element is accomodated in a suitably sized hole in the simple metal lattice. The metal lattice belongs to one of the four types face-centred cubic, body-centred cubic, hexagonal close-packed or simple hexagonal. If r_X/r_{Me} is greater than 0.59 the structures are more complicated. Hägg's conclusions were mainly based on observations of hydrides, carbides and nitrides, few borides being known at that time. The present investigations have shown that as long as boron appears isolated in the metal lattice the borides are

analogous to hydrides, carbides and nitrides. Solid solutions of boron in the expanded lattices of the pure metals have been observed for thorium ($r_B/r_{Th} = 0.48$) zirconium ($r_B/r_{Zr} = 0.54$), titanium ($r_B/r_{Ti} = 0.59$), and tantalum ($r_B/r_{Ta} = 0.60$). For the other metals, all having a ratio greater than 0.59, no solubility has been observed by the present author or is reported in the literature. The systems with tantalum, columbium ($r_B/r_{Cb} = 0.60$) and titanium with a ratio near the critical limit are of special interest. They all seem to have an intermediate position between simple and complicated systems. This is shown by the fact, that simple phases exist at higher temperatures but are transformed to more complicated phases at room temperature. Also for the borides a critical radius ratio thus seems to exist with a value of about 0.59—0.60. The existence of a critical ratio indicates that a simple metal lattice can not be expanded beyond a certain limit. This would imply that the critical limit is also related in some way to the limit of solid solubility in the lattice of the pure metal. The experimental evidence is insufficient, however, to make any conclusions possible. Further experiments are also necessary in order to determine whether the type of metal lattice has any influence on the critical limit r_X/r_{Me}.

The boron atoms, as has been shown, have a marked tendency to form covalent boron-boron bonds. For borides in which the boron atoms are bonded in this way, the limit 0.59 seems to be of less importance. Simple hexagonal metal lattices are thus observed in the borides of AlB_2-type for radius ratios between 0.54 (for zirconium) and 0.69 (for chromium). The dominating factor seems to be the hexagonal boron nets, which easily fit into a simple hexagonal metal lattice. The simple cubic metal lattice, observed for the MeB_6-borides, is probably also only a result of a convenient space arrangement, isolated metal atoms being accomodated in a boron framework.

The stability of the hydrides, carbides, and nitrides decreases with increasing atomic number of the transition elements within a period. Data on the stability of the borides have not been obtained and many of them are apparently inert and stable at higher temperatures. A comparison of the boron contents of the phases of the elements of a period richest in boron shows, however, that the same tendency also seems to exist for the borides. In the first transition period the phases richest in boron have a boron content (in atomic %) of at least 67 for titanium and vanadium, 67 for chromium, 57 for manganese, 50 for iron, cobalt, and probably nickel. Attempts to prepare borides of copper have been hitherto unsuccessful. For the second period, this tendency is less obvious (67 for zirconium and about 70 for columbium and molybdenum) but for the third the same tendency is visible again (86 for lanthanum and some lanthanides, 72 for tantalum and 68 for tungsten).

Finally, it has been confirmed that the borides have metallic properties in analogy with the other members of this group. The results thus verify that the borides of the transition elements may be placed in the same group as the hydrides, carbides and nitrides, but the existence of boron-boron bonds is of importance and must be specially considered.

Application of Pauling's theory. A general theory for the metallic state has been given by Pauling [29–31]. According to this theory, the metallic bond is of the same nature as the covalent bond, but weaker. It thus applies the theory of the electron-pair bond, *dsp*-hybridisation of "pure" *d*, *s*, and *p*-orbitals and resonance. A method for calculation of bond numbers for different bonds and of the valency of different atoms is given, using the interatomic distances. The present author has tried to use this theory for the borides, but without success. If for instance the bond number for the metal-boron bond is calculated for the isomorphous Me_2B-borides, the following values are obtained: 0.28 for tantalum, 0.34 for molybdenum and tungsten, 0.42 for manganese, 0.44 for iron, 0.49 for cobalt, 0.48 for nickel. This increase in bond number may be an indication of an increasing strength of the metal-boron bond, but it may also merely be a consequence of the method of calculation. Although Ta_2B, the boride giving the smallest bond number, is not stable at higher temperatures contrary to the other borides of this group, the difference in bond numbers seems too high. As all these compounds are isomorphous and thus probably energetically similar, it seems rather incredible that such a great variation in bond number for the same metal-boron bond exists. According to a rule, given by Pauling in [31], the bond numbers should have a great tendency to form small integer ratios, *e. g.* 1/2, 1/3, 2/3, 1/4 *etc.* No such tendency is found for the bond numbers discussed, however, the numbers increasing continuously when going from tantalum to cobalt.

Pauling has also used the theory on FeB [31] for which he assumes that electrons are transferred from the iron lattice to the boron to a maximum extent of about one electron per metal atom. The present author has studied all the borides with chain structures in an analogous way. Also for these borides there is a disagreement between isomorphous compounds, and the results can only be interpreted if one assumes that electrons are transferred from the metal lattice to the boron chains. Such an electron transfer is rather difficult to correlate with the properties of the borides with chain structures. All of these borides undoubtedly are metallic and the metallic properties indicate, contrary to Pauling's calculations, that electrons are transferred to the metal lattice from the boron chains and that these borides may be regarded as expanded metal lattices with boron chains in the interstices. These additional

electrons of the metal lattice compensate for the loss in "metallic" properties, which would be a result of the increased metal-metal distance.

The formation of boron chains with covalent boron-boron bonds and an angle between two adjacent bonds of roughly about 120° is also difficult to explain, if electrons were transferred to the chains from the surrounding metal lattice. The electron configuration of a boron atom is $1s^2 2s^2 2p^1$, thus with three electrons in the second quantum level. If electrons are transferred to the boron chains, which appears according to Pauling, each boron atom would get between three and four electrons available for bond formation. With nearly four electrons per atom, however, a tendency for boron-boron double bonds would probably be visible. Neither the boron-boron distance observed nor the angle of about 120° between the bonds formed are compatible with this view. A double bond is considerably shorter than the distances observed, and the angle between two double bonds formed by the same boron ion probably would be 180°, by analogy with carbon. On the contrary a loss of electrons is more in accordance with the existence of covalent bonds within the chains. If in the ideal case one electron per boron atom is lost to the metal lattice, two electrons would be left, which is exactly the number necessary for each boron to form two covalent single bonds. It is thus more probable that a chain of the kind existing would be stabilized by a loss of electrons from the boron than by a transfer of electrons to the boron.

It is also of interest to note that Engel has put forth a theory for the electron distribution in metal lattices [32] which is in accordance with the above assumption. According to this theory, a body-centred metal lattice is characterized by an electron concentration of one ($s + p$)-electron per metal atom, an hexagonal close-packed lattice by two such electrons and a cubic close-packed lattice by three. Regarding the metal lattice of the borides of CrB-type, an obvious relationship between this lattice and an hexagonal close-packed lattice is noted (Fig. 5), although the former is very deformed. The metal lattices of the other two boride types with chains (MoB- and FeB-types), are similar to the CrB-lattice. If the present author's opinion of the electron transfer in these borides is correct, in the ideal case one electron per boron atom would be transferred from the boron chains to the metal lattice and the electron concentration of the metal would increase by one electron per metal atom. The borides with boron chains are formed by the metals chromium, columbium, tantalum, molybdenum, tungsten, manganese, iron and cobalt. All these metals at room temperature crystallize with cubic body-centred lattices with the exception of manganese and cobalt. Manganese, however, has a lattice not so different from the body-centred arrangement whereas cobalt is known in an hexagonal close-packed as well as a cubic close-packed modification. By

Fig. 5. Metal lattice of CrB (left) projected on the ab-plane, compared with an hexagonal close-packed metal lattice (right).

electron transfer from the boron chains in these borides, the electron concentration of the metal lattice increases. The borides of metals with a body-centred structure thus will have a tendency to possess an hexagonal close-packed metal lattice in accordance with the experimental evidence. Cobalt boride is the only exception, but it is to be noted that the axial ratio for CoB is considerably different from that of the isomorphous MnB and FeB ($a:b:c$ = 1.87 : 1 : 1.39 for MnB, 1.87 : 1 : 1.38 for FeB but 1.73 : 1 : 1.30 for CoB). Titanium and zirconium, which both crystallize in hexagonal close-packed lattices at room temperature, do not give any boride phases with boron chains. Nor have such phases been observed for copper or nickel with cubic close-packed lattices, in accordance with the view expressed above.

It is also of interest to compare these borides with Cr_3C_2[33] ($D\ 5_{10}$), the only known carbide with carbon chains. The lattice of this carbide is in many respects related to that of FeB, and it has zig-zag shaped carbon chains with a carbon-carbon distance of the order of magnitude of a single bond. Such a chain would in the ideal case be stabilized by a loss of two electrons per carbon atom to the metal lattice. The content of non-metallic element thus should be lower than the 50 atomic % found for boron, if the electron concentration of the metal lattices is of the same order of magnitude, in accordance with the experimental evidence.

Finally an electron transfer from the chains to the metal lattice would also account for the similarities in physical properties between these borides and the true interstitial compounds, where an electron transfer in the direction mentioned in some instances has been experimentally verified. The case of positive hydrogen in metal hydride lattices is wellknown. An electron transfer from the interstitial atoms to the metal lattice has also been suggested to occur in the ε and ζ carbonitrides of iron [34]. The effective atomic radius of carbon is less than that of nitrogen in these compounds. Since carbon replaces nitrogen within wide limits, without any marked structural change, each carbon atom is assumed to lose the same number of electrons (or the same fraction of an electron) as a nitrogen atom. The relative loss of electrons would thus be

greater for carbon than for nitrogen and might account for the smaller effective radius of carbon.

The experimental evidence thus indicates, according to the present author's opinion, that in the borides with boron chains there is an electron transfer from the chains to the metal lattice, contrary to Pauling's theory. There is a possibility that all these borides are to be regarded as chain analogs to the true interstitial compounds with isolated interstitial atoms. As the tendency for the chains to lose electrons is greater than for isolated atoms, the importance of Hägg's radius ratio is less in the former case. For the borides with double chains and nets, all or nearly all of the electrons of boron are engaged in the formation of boron-boron bonds, and the electron transfer boron-metal is probably small. The simple metal lattices observed for these borides are merely a result of a convenient space arrangement by which the metal-metal coordination still remains high. They have metallic properties, but Hägg's radius ratio is of no importance.

SUMMARY

A comprehensive discussion of the structural work on the borides of the transition elements is given, including tables of axial lengths and interatomic distances. The structures are discussed with respect to the arrangement of the boron atoms.

The boron atoms appear isolated, in chains, in double chains, in nets or in three-dimensional boron frameworks. The crystallographic evidence clearly shows that the boron-boron contacts are of bonding character.

Similarities between borides and hydrides, carbides, and nitrides exist, but Hägg's critical radius ratio is valid only if the boron atoms appear isolated in the metal lattices.

Pauling's theory for the metallic state seems not to be applicable to the borides. For the borides with chains, for instance, according to Pauling an electron transfer from the metal to the boron chains occurs. The present author thinks, according to the experimental evidence, that an electron transfer in the opposite direction is more probable.

The present investigation of the metallic borides has been carried out at the Institute of Chemistry, University of Uppsala, during the years 1945—1949. I here wish to express my gratitude to my inspiring teacher, Professor G. Hägg, for suggesting the work, for valuable discussions and for never failing support. I am also very grateful to my colleagues at the Institute for stimulating discussions and good fellowship. My thanks are due to several students for valuable help, to Mrs. M. Englund and Mr. R. Nordlund for

preparing the figures in this and preceeding papers and to Mr. S. Wahlgren for technical assistance. This investigation has been supported continously by the *Swedish State Council of Technical Research*, which support is gratefully acknowledged.

REFERENCES

1. Kiessling, R. *Acta Chem. Scand.* **1** (1947) 893.
2. Kiessling, R. *Ibid.* **3** (1949) 90.
3. Kiessling, R. *Ibid.* **3** (1949) 595.
4. Kiessling, R. *Ibid.* **3** (1949) 603.
5. Kiessling, R. *Ibid.* **4** (1950) 146.
6. Andersson, L. H., and Kiessling, R. *Ibid.* **4** (1950) 160.
7. Hansen, M. *Der Aufbau der Zweistofflegierungen.* Berlin (1936).
8. Haughton, J. L. *Inst. Metals (London), Monograph Rep. Ser. No. 2* (1942).
9. Bjurström, T. *Arkiv Kemi, Mineral. Geol.* **A 11** (1933) nr 5.
10. Hägg, G. *Z. physik. Chem.* **B 11** (1930) 152.
11. Hägg, G. *Ibid.* **12** (1931) 413.
12. Ehrlich, P. *Z. anorg. Chem.* **259** (1949) 1.
13. Hofmann, W., and Jänniche, W. *Z. physik. Chem.* **B 31** (1936) 214.
14. McKenna, P. M. *Ind. Eng. Chem., Ind. Ed.* **28** (1936) 767.
15. Norton, J. T., Blumenthal, H., and Sindeband, S. J. *J. Metals.* **1** (1949) 749.
16. Allard, G. *Bull. soc. chim. France* **51** (1932) 1213.
17. v. Stackelberg, U., and Neumann, F. *Z. physik. Chem.* **B 19** (1932) 314.
18. Laves, F. *Ibid.* **22** (1933) 114.
19. Pauling, L., and Weinbaum, S. *Z. Krist.* **87** (1934) 181.
20. Hocart, R., and Fallot, M. *Compt. rend.* **203** (1936) 1062.
21. Halla, F., and Thury, W. *Z. anorg. u. allgem. Chem.* **249** (1942) 229.
22. Sindeband, S. J. *J. Metals* **1** (1949) 198.
23. Bertaut, F., and Blum, P. *Compt. rend.* **229** (1949) 666.
24. Kiessling, R. *Acta Chem. Scand.* **2** (1948) 707.
25. Kiessling, R. *Tek. Tid.* **77** (1947) 586.
26. Kiessling, R. *Jernkontorets Ann.* **132** (1948) 237.
27. Hägg, G. *Z. physik. Chem.* **B 6** (1929) 221.
28. Hägg, G. *Ibid.* **12** (1931) 33.
29. Pauling, L. *Phys. Rev.* **54** (1938) 899.
30. Pauling, L. *J. Am. Chem. Soc.* **69** (1947) 542.
31. Pauling, L. *Proc. Roy. Soc. London* **A 196** (1949) 29.
32. Engelo N. *Kem. Maanedsblad* **30** (1949) 53.
33. Hellb,m, K., and Westgren, A. *Svensk Kem. Tid.* **45** (1933) 141.
34. Jack, K. H. *Proc. Roy. Soc. London* **A 195** (1948) 41.

Received January 28, 1950.

Printed in Finland by Frenckellin Kirjapaino Osakeyhtiö, Helsinki.